Site-Specific Excited-State Solute-Solvent Interactions Probed by Femtosecond Vibrational Spectroscopy

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Solute-solvent interactions in liquids are studied by femtosecond vibrational spectroscopy. Upon electronic excitation, the C=O stretching band of an organic probe molecule, a coumarin dye, dissolved in $CHCl_3$ shows a strong blueshift on a 200 fs time scale. This demonstrates for the first time the cleavage of a site-specific intermolecular hydrogen bond with a polar solvent. After this fast process, the picosecond reorganization of the solvent due to dielectric relaxation is directly monitored via changes of the C=O vibrational frequency. [S0031-9007(98)07298-6]

Solute-solvent interactions play a fundamental role for molecular nonequilibrium processes in liquids. They govern the ultrafast optical dynamics of vibronic excitations and many chemical reactions. Optical dephasing and solvation dynamics have been studied via the transient Stokes shift of fluorescence from probe molecules [1] and by coherent techniques [2]. In many cases, solvation dynamics consist of ultrafast (100–200 fs) and slower picosecond components which have been analyzed in molecular dynamics simulations. The degree and time scales of solvation depend not only on the solvent but also strongly on specific solute properties such as size, polarizability, charge distribution in the ground and excited states, as well as solute motion [3,4].

Most of the experimental techniques applied so far give limited information on local solute-solvent geometries and—thus—provide only limited insight into the microscopic mechanisms. This is due to the fact that such experiments are sensitive only to an ensemble-averaged two-point time-correlation function for liquid motions. In time-resolved emission measurements one observes the correlation function $S(t)$ of solvation dynamics [5],

$$S(t) = \frac{\omega_{el}(t) - \omega_{el}(\infty)}{\omega_{el}(0) - \omega_{el}(\infty)}, \tag{1}$$

where $\omega_{el}(t)$ is the electronic transition frequency between the ground and excited-state charge distributions. Within the linear response approximation $S(t)$ is identical to the normalized correlation function $C(t)$,

$$C(t) = \frac{\langle \delta\omega_{el}(t)\delta\omega_{el}(0)\rangle}{\langle \delta\omega_{el}(0)^2\rangle}, \tag{2}$$

where $\langle X \rangle$ denotes an ensemble average of the quantity X; $\delta\omega_{el}$ denotes a fluctuation in the energy difference $\delta\omega_{el} = \omega_{el} - \langle\omega_{el}\rangle$. The correlation function $C(t)$ also determines the dynamics observed in various coherent four-wave mixing experiments. $C(t)$ lacks information on nuclear coordinates, spatial dependencies, and specific local solute-solvent interactions [6]. Thus, new experimental methods are required to get better insight into the microscopic molecular motions. Recently, low-frequency

vibrational and librational motions have been studied by fifth-order Raman spectroscopy [7] and by visible pump, terahertz probe spectroscopy [8].

Intermolecular hydrogen bonding between solute and solvent represents an important type of local interaction mechanisms that are expected to occur in many polar protic solvents and to strongly influence dephasing and solvation on ultrafast time scales. Until now, the role of hydrogen bonds has barely been characterized both by theory and experiment. Here, femtosecond vibrational spectroscopy which has been used to monitor chemical reactions [9] should provide information on local structures. In this Letter, we introduce femtosecond vibrational spectroscopy of the solute as a sensitive probe to the dynamics of site-specific hydrogen bonding. The dynamics of hydrogen bonds between solute and solvent are studied by electronically exciting the solute and probing stretching vibrations of characteristic functional groups with femtosecond time resolution. We demonstrate for the first time that the C=O group of coumarin chromophores [10] in a polar hydrogen donating environment is part of a hydrogen bond which breaks after electronic excitation within a 200 fs time scale, followed by picosecond reorientation dynamics of the solvent shell.

In our experiments we study coumarin 102 (C102) dissolved in nonpolar C_2Cl_4 and in polar $CHCl_3$. The electronic absorption and emission spectra (Fig. 1) are different for the two solvents, indicating strong changes of solute-solvent interactions in going from C_2Cl_4 to $CHCl_3$ [5]. Vibrational spectra of C102 in the electronic ground state are shown in Fig. 2 (solid lines). In C_2Cl_4 the C=O stretching band of C102 occurs around 1735 cm^{-1}, characteristic of a free C=O group. The small splitting of this band has been assigned to a Fermi resonance [11]. In contrast, the C=O band of C102 in $CHCl_3$ is strongly downshifted to 1700 cm^{-1}, indicating a strong hydrogen bond between solute and solvent with a binding energy of $8-15$ kJ mol^{-1} [12].

In the femtosecond pump-probe measurements C102 is excited to the S_1 state by a 100 fs pulse at a wavelength $\lambda_{ex} = 395$ and $\lambda_{ex} = 405$ nm for C102 in C_2Cl_4 and
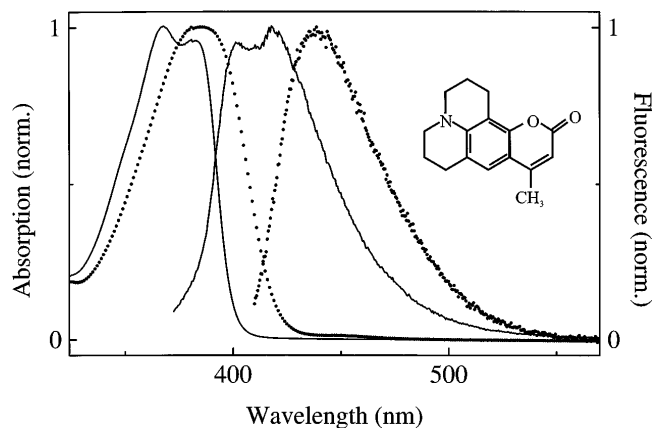
FIG. 1. Electronic absorption and emission spectra of C102 in C_2Cl_4 (solid lines) and $CHCl_3$ (dots). Inset: Molecular structure of coumarin 102 (C102).

$CHCl_3$, respectively. The change of the vibrational spectra upon electronic excitation is probed by 130 fs pulses tunable in the midinfrared from 1500 to 1780 cm^{-1} (λ_{probe} = 5.7 to 6.7 μm). Pump and probe pulses are derived from an amplified Ti:sapphire laser system by frequency doubling and a parametric infrared generation [13], respectively. Pump and probe pulses are focused in a 200 μm thick jet of a 0.005 M solution of C102. From the energy absorbed per excitation pulse, the excited volume and concentration of the sample, we estimate that a fraction $\eta = 0.30 \pm 0.05$ of the C102 molecules are excited to the S_1 state [14]. The time resolution of the experiment is 200 fs.

In Fig. 2, we present transient infrared spectra of C102 recorded 10 ps after electronic excitation. In Figs. 2(b) and 2(d), we plot the change of absorbance $\Delta A(\nu) = -\log\{[T(\nu) - T_0(\nu)]/T_0(\nu)\} = -\eta A_{S0}(\nu) + \eta A_{S1}(\nu)$, where $T_0(\nu)$ and $T(\nu)$ are the infrared transmissions

of the sample before and after electronic excitation, respectively. $A_{S0}(\nu)$ and $A_{S1}(\nu)$ represent the infrared absorbance in the S_0 and S_1 state, respectively. For the nonpolar solvent C_2Cl_4, $\Delta A(\nu)$ [Fig. 2(b)] shows a strong bleaching at the positions of the C=O stretching band and of the ring mode at 1610 cm^{-1}. The circles in Fig. 2(a) give the transient spectrum $A_{S1}(\nu)$ of excited molecules derived from the measured quantities $\Delta A(\nu)$, $A_{S0}(\nu)$, and η. $A_{S1}(\nu)$ demonstrates a decrease of the vibrational transition moments without significant spectral shifts. For the polar solvent $CHCl_3$ [Figs. 2(c) and 2(d)] the ring mode also exhibits a transient bleaching. More importantly, we observe a strong bleaching of the ground-state C=O stretching band and the appearance of a new band up-shifted to 1746 cm^{-1} in the excited state. This C=O band is located at about the same spectral position as that in C_2Cl_4, where a free C=O group exists, indicating a much weaker hydrogen bonding interaction between the C=O group and $CHCl_3$.

In Fig. 3, we present time-resolved data for different spectral positions of the probe pulses. At the maximum of the ground-state C=O stretching band in the two solvents [Figs. 3(a) and 3(b)] and of the 1610 cm^{-1} mode (not shown), one finds a bleaching of the initial absorption which rises at negative delay times, reaches a maximum value around 0.5 ps, and decays very slowly on a time scale of hundreds of picoseconds, the excited state life-
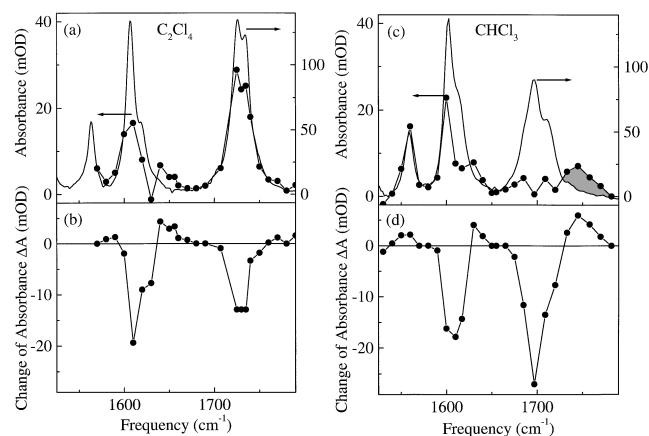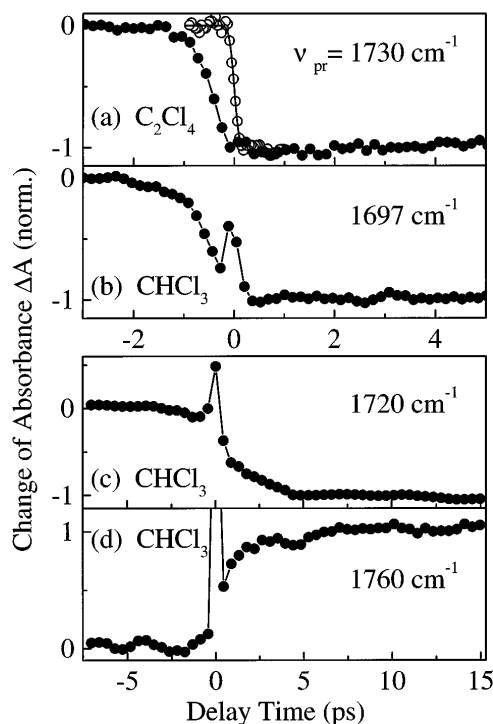

FIG. 2. Ground-state infrared spectrum $A_{S0}(\nu)$ (solid lines, right ordinate scales) and excited-state spectrum $A_{S1}(\nu)$ (circles, left ordinate scales) of C102 in (a) C_2Cl_4 and (c) $CHCl_3$. The excited-state spectra are derived from the change of infrared absorbance $\Delta A(\nu)$ in (b) and (d) which was measured at a delay time of 10 ps.

FIG. 3. Spectrally and temporally resolved absorbance changes of C102 in (a) C_2Cl_4 and (b), (c), and (d) $CHCl_3$ after electronic excitation (solid circles). The spike near zero delay is due to a coherence effect. The open circles represent the cross correlation of pump and probe. Note the different abscissa scales of (c) and (d).

time of C102 (solid circles). The open circles in Fig. 3(a) represent the time-integrated cross correlation function of pump and probe derived from the infrared absorption of a photogenerated electron-hole plasma in silicon. The solute signals at negative delay times, i.e., when the probe pulse interacts with the sample before the pump, are due to the perturbed free induction decay of the infrared polarization created resonantly on the vibrational transition [15]. The transients in Figs. 3(c) and 3(d) were measured with C102 in CHCl$_3$. At 1720 cm^{-1}, one probes both the bleaching of the ground-state C=O band and the absorption increase due to the excited-state C=O band. The overall signal shows a bleaching with an initial appearance within 200 fs, followed by a slower component with a time constant of 2.5 ± 0.3 ps [16]. The absorption increase at 1760 cm^{-1} [Fig. 3(d)] exhibits a similar fast rise, followed by the slower component. Measurements at different spectral positions indicate that the slower kinetics reflect a blueshift of the C=O stretching band in the excited state by $\Delta\tilde{\nu} = 7$ cm^{-1}. This is evident from Fig. 4, where the measured first moment of the new vibrational band, $M(\tau) = \Delta\tilde{\nu}_{sol}(t) = \int \tilde{\nu} F(\tau, \tilde{\nu}) d\tilde{\nu}$, $F(\tau, \tilde{\nu})$: time-dependent C=O band in S_1, is plotted versus delay time τ. $M(\tau)$ is equal to the time-dependent vibrational frequency shift $\Delta\tilde{\nu}_{sol}(t)$ after excitation.

We now consider the microscopic mechanisms responsible for the transient changes of the infrared spectra. Excitation to the S_1 state results in a redistribution of electronic charge in the solute occurring within the time resolution of our experiments. The charge redistribution has the following effects: (i) A change of the—in general anharmonic—potential energy surfaces of the normal modes and infrared dipole moments of the solute, i.e., vibrational oscillator strengths may change; (ii) changes in the site-specific interaction between the solute and the sol-

vent affecting the vibrational bands of specific functional groups of the solute; (iii) a reorientation of the solvent shell in polar surroundings. Our experiments give—for the first time—specific insight into all three effects. In the nonpolar solvent C$_2$Cl$_4$, the solute-solvent interaction is weak, and changes of the vibrational spectra are dominated by the intramolecular charge redistribution. In this case, the infrared spectra in the S_1 state show a substantial instantaneous decrease of vibrational oscillator strength and—if at all—frequency shifts which are much less than the vibrational linewidths of the ring mode at 1610 cm^{-1} and the C=O mode at 1735 cm^{-1}. For C102 in the polar solvent CHCl$_3$, the ring mode shows a similar behavior. We conclude that the changes of vibrational force constants by charge redistribution are very small. In contrast, the solute-solvent interaction is strong in the polar CHCl$_3$. Here, the C=O mode of C102 exhibits a rapid change of force constant within 200 fs. The vibrational frequency increases by 38 cm^{-1} in the S_1 state and is characteristic of a free C=O group. This demonstrates a cleavage of the hydrogen bond between the C=O group and the solvent, i.e., a pronounced change of the site-specific solute-solvent interaction. The time scale of cleavage is determined by low-frequency motions of the hydrogen bonded groups in the 100 to 200 cm^{-1} range.

This qualitative argument is supported by semiempirical calculations of electronic charge distributions in the S_0 and S_1 states of C102. The calculations show that upon excitation the C=O moiety becomes slightly less polar and the negative charge on the O atom decreases, similar to other coumarin dyes [3]. This leads to a decrease in affinity for hydrogen bonding between the carbonyl oxygen atom of C102 and the solvent upon electronic excitation.

We now discuss the small additional shift of the C=O band of 7 cm^{-1} that occurs on a time scale of 2.5 ps in CHCl$_3$. These dynamics take place after the fast disappearance of the hydrogen bond and reflect the reorientation of the solvent shell. It has been shown that solvent shifts of vibrational frequencies can be modeled fairly well using Onsager's approach of a point dipole to represent the probe molecule embedded in a spherical cavity surrounded by a continuous solvent medium with a macroscopic dielectric constant [17]. In this model, it is possible to derive the equivalent of the van der Zwan–Hynes relation for the time-resolved vibrational frequency shift after electronic excitation. We implement a time-dependent reaction field induced by a point dipole altered by electronic excitation [18] into the potential function for the molecular vibration coupled to the molecular dipole moment. We then follow Pullin's derivation for the solvent induced vibrational frequency shift $\Delta\tilde{\nu}_{sol}$ [17] and straightforwardly calculate the time-dependent solvent induced vibrational frequency shift $\Theta(t)$,
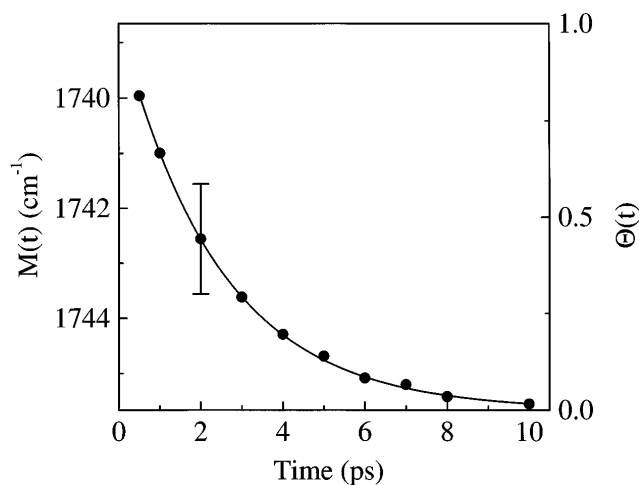

FIG. 4. Long time behavior of the normalized first order moment $M(t)$ of the transient C=O band as a function of pulse delay (circles). $M(t)$ and the vibrational frequency shift $Q(t)$ reflect the time evolution of the dielectric friction function. Solid line: Exponential decay of 2.5 ± 0.3 ps.

$$\Theta(t) = \frac{\Delta\tilde{\nu}_{sol}(t) - \Delta\tilde{\nu}_{sol}(\infty)}{\Delta\tilde{\nu}_{sol}(0) - \Delta\tilde{\nu}_{sol}(\infty)} = 1 - z(t). \quad (3)$$

where the solvation coordinate $z(t)$ is defined by Eq. (2.19) of Ref. [18]. It follows that $\Theta(t)$ is identical to the time-resolved fluorescence Stokes shift $S(t)$ [Eq. (1)] and the time-dependent dielectric friction function [18]. Often one describes the dielectric response of the solvent by a Debye form,

$$\Theta(t) = \exp\left[-\frac{2\epsilon_0 - \epsilon_\infty}{3\epsilon_\infty}\frac{t}{\tau_D}\right] = \exp\left[-\frac{t}{\tau_\nu}\right], \quad (4)$$

where ϵ_0 and ϵ_∞ are the dielectric constants at zero and optical frequencies, respectively, and τ_D is the Debye relaxation time. By assuming that $\epsilon_\infty = n^2$, where n is the index of refraction at the infrared wavelength, we calculate the ratio of $\tau_{\nu,\mathrm{IR}}$ at the infrared wavelength to $\tau_{\nu,\mathrm{VIS}}$ at optical wavelengths to be equal to 0.89. Notwithstanding the fact that dielectric response functions usually exhibit multiexponential decay behavior, we can use the averaged experimental value for $\tau_{\nu,\mathrm{VIS}} = 2.8$ ps [5] and estimate a dielectric relaxation constant in the infrared to be $\tau_{\nu,\mathrm{IR}} = 2.5$ ps. This is in excellent agreement with our experimental result shown in Fig. 4.

In conclusion, we have shown that femtosecond vibrational spectroscopy is a unique tool to probe the dynamics of site-specific interactions between a probe molecule and the solvent. We experimentally determined the time scales of changes in intermolecular hydrogen bonding after electronic excitation. In the case of coumarin 102, a member of the class of widely used coumarin probes for solvation dynamics, we show that the hydrogen bond with $CHCl_3$, effective in the electronic ground state, is broken within 200 fs after electronic excitation of the probe molecule. We note that this is the same time scale when the so-called inertial part of the solvation response takes place. As hydrogen bonding occurs in a wide range of solvents, our results have far-reaching consequences for interpretation of solvation studies. In addition we connect additional dynamics of the free C=O stretching mode on a time scale of 2.5 ps to the dielectric response of the solvent.

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